INNOVATIVE TECHNOLOGY
Summary Report

Induced Fluorescence Sensors for Direct Push Systems

Characterization, Monitoring, and Sensor
Technology
Crosscutting Program and
Subsurface Contaminants Focus Area

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Induced Fluorescence Sensors for Direct Push Systems

Tech ID 2237

Characterization, Monitoring, and Sensor Technology
Crosscutting Program and
Subsurface Contaminants Focus Area

Demonstrated at
Savannah River Site
Aiken, South Carolina

Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine whether a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

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SECTION 1
SUMMARY

Technology Summary

Subsurface contamination by petroleum oils and lubricants (POLs) and non-aqueous phase liquids (NAPLs) presents a serious challenge in the cleanup of many DOE, DoD, and other government and civilian facilities. Of particular concern to DOE are dense non-aqueous phase liquids (DNAPLs), primarily chlorinated hydrocarbons used as cleaning and degreasing agents. These hazardous constituents dissolve only sparingly in water. In the subsurface they tend to form blobs and ganglia which disperse and sink; their subsurface migration is less directly connected to groundwater flow than is the case with more soluble pollutants. Once introduced into the subsurface they can remain as sources of contamination for extremely long periods. Delineating the extent of contamination is a necessary first step toward remediation. This delineation is a major challenge due to the typically dispersed nature of the contamination. The goal is to locate and then remediate or isolate the non-aqueous phase sources; once this is done, groundwater contamination by these constituents can be remediated by other means including monitored natural attenuation.

The Department of Energy's (DOE) Subsurface Contaminants Focus Area (SCFA) and the Character-ization, Monitoring, and Sensor Technology Crosscutting Program (CMST-CP), along with others in the DOE, the Department of Defense (DoD), the U.S. Environmental Protection Agency (U.S. EPA), other research organizations, and industry, have worked to identify and develop innovative technologies for this purpose. A number of these form the SCFA's **DNAPL Characterization Toolbox** (TechID 237); see Rossabi *et al.* 2000a. Many sensors in this toolbox may be deployed using direct push systems such as the Cone Penetrometer (TechID 243), providing greatly reduced sampling and analysis costs over traditional soil borings. Additional benefits of direct push sensor deployments include obtaining real-time, continuous readings during a push, avoiding the generation of secondary waste, and avoiding sample handling and shipping.

Induced fluorescence sensors can be efficient screening tools for the presence of certain POLs and NAPLs. The subsurface media adjacent to the probe are illuminated with ultraviolet light. Polycyclic aromatic hydrocarbons (PAHs), if present, will fluoresce in response to this illumination. This fluorescence is usually transmitted via a fiber-optic cable to a spectrometer or other sensor at the surface. PAHs are commonly found in POLs and certain other organic constituents such as coal tar derivatives. DNAPLs themselves will not fluoresce when excited at feasible wavelengths. In many cases, however, PAHs are found in DNAPLs that have been used in cleaning or degreasing operations (Kram *et al.* 1996, 1997a, 1998, 2001, 2002; Keller and Kram, 1998). Depending on the excitation wavelength(s) of the ultraviolet illumination source, fluorescence may in principle also be obtained from aromatic hydrocarbons with only one or two rings, although in field applications this fluorescence will tend to be dwarfed by that from PAHs with three or more rings. Hence, preliminary evaluation is needed to determine which of these techniques, if any, will be useful for detecting the particular contaminant of concern at each site.

The induced fluorescence will have distinct frequency and time spectra depending on the PAHs present and on the exciting frequency. Frequency and/or time domain analyses of the observed fluorescence can be used to distinguish among categories of fluorescing compounds, such as distinguishing fuels from coal tar residues and distinguishing hydrocarbon contamination in general from natural mineral fluorescence. Recent developments utilizing multiple excitation and response frequencies show promise at both identifying and quantifying multiple individual constituents of concern (Kenny *et al.* 2000).

A number of commercial and other realizations of this principle exist. Those described in this report are the following:

- the Rapid Optical Screening Tool (ROST™) developed by Dakota Technologies, Inc. (DTI) and marketed by DTI and Fugro Geosciences, Inc.;

- the Fuel Fluorescence Detector (FFD™) developed and marketed by Applied Research Associates (ARA); and

- the Site Characterization and Analysis Penetrometer System (SCAPS) Laser-Induced Fluorescence (LIF) Sensor developed by the RDT&E Division of the Naval Command, Control and Ocean Surveillance Center in collaboration with the U.S. Army Waterways Experimental Station and Army Environmental Center and others including DOE.

Figure 1 shows DTI's concept of the screening process. The cone penetrometer (CPT) pushes the probe through the subsurface, obtaining nearly continuous readings of total fluorescence. The regions of high fluorescence correspond to contaminated layers in the subsurface. The fluorescence spectrum obtained at a particular depth indicates the nature of the contaminant present.
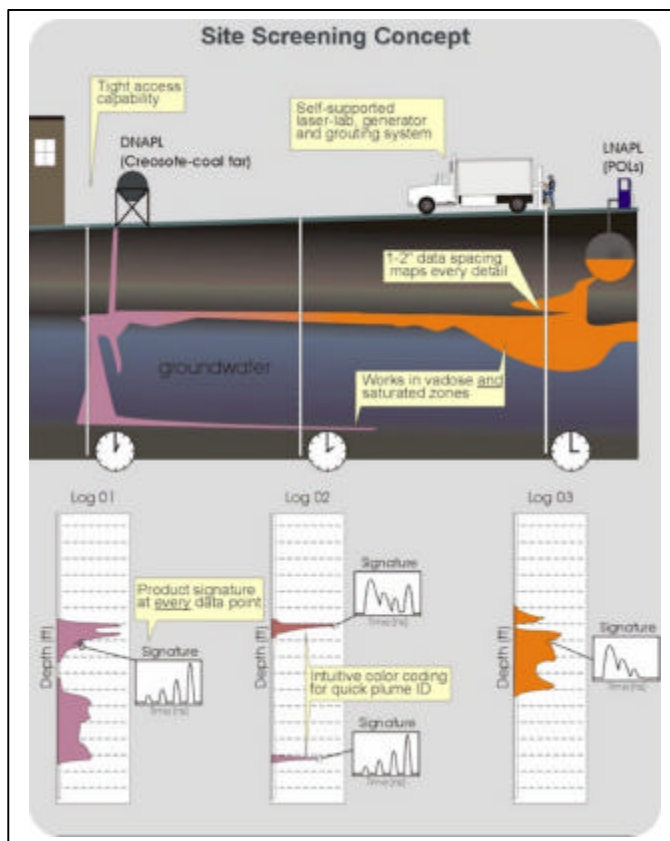

Figure 1. Soil screening for POLs and NAPLs using ROST^TM; from www.dakotatechnologies.com, used with permission. The data logs show total fluorescence; different spectral signatures distinguish different sources of contamination.

Demonstration Summary

This ITSR focuses on the demonstration of the use of the ROST[TM] for DNAPL screening which took place at the Savannah River Site M-Area Settling Basin, Aiken, South Carolina (SRS) during 1998. This is the basis for the cost analyses of Section 5. Induced fluorescence techniques were also included in demonstrations of DNAPL characterization techniques at the SRS 321-M Solvent Storage Tank Area during 1998 and at the NASA Launch Complex 34 site at Cape Canaveral Air Station during 1999; these techniques were not successful in this demonstration because of the absence of fluorescing PAHs in the subsurface DNAPLs.

Demonstrations of screening for POLs using these techniques were conducted previously by U.S. EPA's National Exposure Research Laboratory (NERL) at the Hydrocarbon National Test Site located at the Naval Construction Battalion Center, Port Hueneme, California (May 1995) and the Steam Plant Tank Farm at Sandia National Laboratories, Albuquerque, New Mexico (November 1995). NERL has published *Innovative Technology Verification Reports* on the systems evaluated, which were the SCAPS LIF Sensor (Bujewski and Rutherford 1997a) and the ROST[TM] system (Bujewski and Rutherford 1997b). NERL's conclusions are summarized briefly in Section 3.

These demonstrations show that these techniques are useful as screening tools for POLs. Their usefulness in screening for NAPLs depends on the presence of PAHs in lubricants dissolved in the NAPLs for their fluorescence. Kram *et al.* (2001) state that a concentration of only 1% PAH or other fluorescing compound in NAPL is sufficient; Rossabi (personal communication) states that the minimum concentration of 200-300 ppm at best will work. These are screening tools. Quantitation is approximate, since the strength of fluorescence depends on the concentration of PAHs in the particular contaminant involved. Calibration using the site-specific contaminant is required to achieve any quantitation at all. Further, the fluorescence intensity depends also on the nature of the soils present. Moreover, NAPLs present in the subsurface will be dispersed into blobs and ganglia. Since the sensor will measure only the fluorescence of materials in the optical path, concentration measurements inherently disregard the heterogeneous nature of contaminant dispersion.

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Other

All published Innovative Technology Summary Reports are available on the OST Web site at www.em.doe.gov/ost under "Publications." The Technology Management System (TMS), also available through the OST Web site, provides information about OST programs, technologies, and problems. The TechID for Induced Fluorescence Sensors for Direct Push Systems is 2237.

SECTION 2
TECHNOLOGY DESCRIPTION

Overall Process Definition

Three hardware systems are involved in searching for POLs or NAPLs using induced fluorescence sensors with direct push systems:

- The delivery system such as a cone penetrometer system.

- The source illumination, either a laser at the surface sending ultraviolet light downhole through a fiber-optic cable or an ultraviolet light source (microchip laser or lamp) in the downhole hardware.

- A sensor located at the surface, which receives the fluorescence via fiber-optic cable, or a downhole sensor system, along with associated processing and recording hardware and software.

Figure 2 shows a cone penetrometer truck in operation. Figure 3 shows a typical cone penetrometer laser induced fluorescence (LIF) sensor with a hard sapphire window through which both the illumination and induced fluorescence pass, along with a schematic diagram of the whole system. The cone penetrometer diameter is usually 1.75". The probe is typically advanced slowly (~2 cm/sec) through the subsurface using hydraulic pressure; measurements taken frequently (up to ten times a second) provide a nearly continuous record of observed fluorescence. Alternately, the probe can be advanced to discrete depths at which measurements are made.

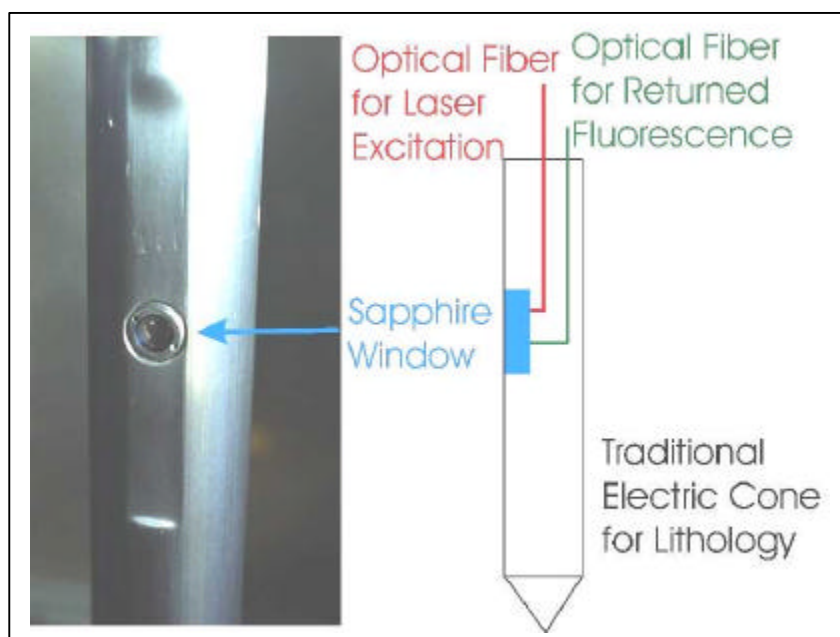**Figure 2. Applied Research Associates's Cone Penetrometer Truck**

Figure 3. Photo and Schematic Diagram for LIF Probe

Different realizations of this concept use different illumination sources. Examples include:

- The ROST^{TM} illumination source, located at the surface, consists of a primary neodymium-doped yttrium aluminum garnet (Nd:YAG) pump laser feeding a tunable rhodamine dye laser. This system produces pulsed ultraviolet (UV) light, typically tuned to a wavelength of 290nm. This UV light is conducted downhole via a fiber-optic cable to illuminate the subsurface.

- The FFD^{TM} uses a downhole mercury lamp with filters producing UV light at approximately 254 nm wavelength.

- The SCAPS LIF Sensor uses a pulsed nitrogen laser emitting UV light at 337nm wavelength at the surface, with the illumination being transmitted downhole via fiber-optic cable.

There are tradeoffs in the selection of the illumination source. Longer wavelength (lower frequency) UV light is more easily transmitted via fiber-optic cable, whereas shorter wavelength light is more energetic and induces fluorescence in a broader class of PAHs. Specifically, at the 337nm excitation wavelength provided by the SCAPS LIF N$_2$ laser fluorescence is exhibited by PAHs containing three or more benzene rings; at 308nm (provided by a xenon chloride laser) and 290nm (the ROST^{TM} wavelength) fluorescence is obtained also from two-ringed PAHs. The ROST^{TM} system can in principle be tuned to 266nm to induce fluorescence from single-ring aromatic compounds as well, such as the BTEX (benzene, toluene, ethylbenzene, and xylene) common in petroleum products. The attenuation of 266nm illumination by the fiber-optic cable is greater than at longer wavelengths, however, so the use of this wavelength with a laser at the surface is limited to shallower pushes. An alternative is to incorporate a microchip laser downhole delivering 266nm UV illumination.

As an illustration of how illuminating energy at different wavelengths is absorbed, Rossabi and Nave (1998) present the absorbance spectra of tetrachloroethylene (perchloroethylene, PCE), a DNAPL commonly used as a degreasing agent, mixed with different amounts of contaminant DNAPL extracted from wells in SRS's M-Area Settling Basin. Figure 4, based on Rossabi and Nave 1998, presents the measured spectra for pure PCE and for PCE containing approximately 200 ppm of hydraulic oils. The energy absorbance of pure PCE is greatest at around 270nm, whereas that of PCE mixed with M-Area DNAPL peaks around 290-300nm. Both show substantial absorbance at the 266 nm wavelength. The latter still shows considerable absorbance at the 337nm wavelength used by the SCAPS LIF system; the former does not. (It has been suggested, however, that the absorbance peak for pure PCE represents absorption by the quartz cuvette rather than the PCE itself.)
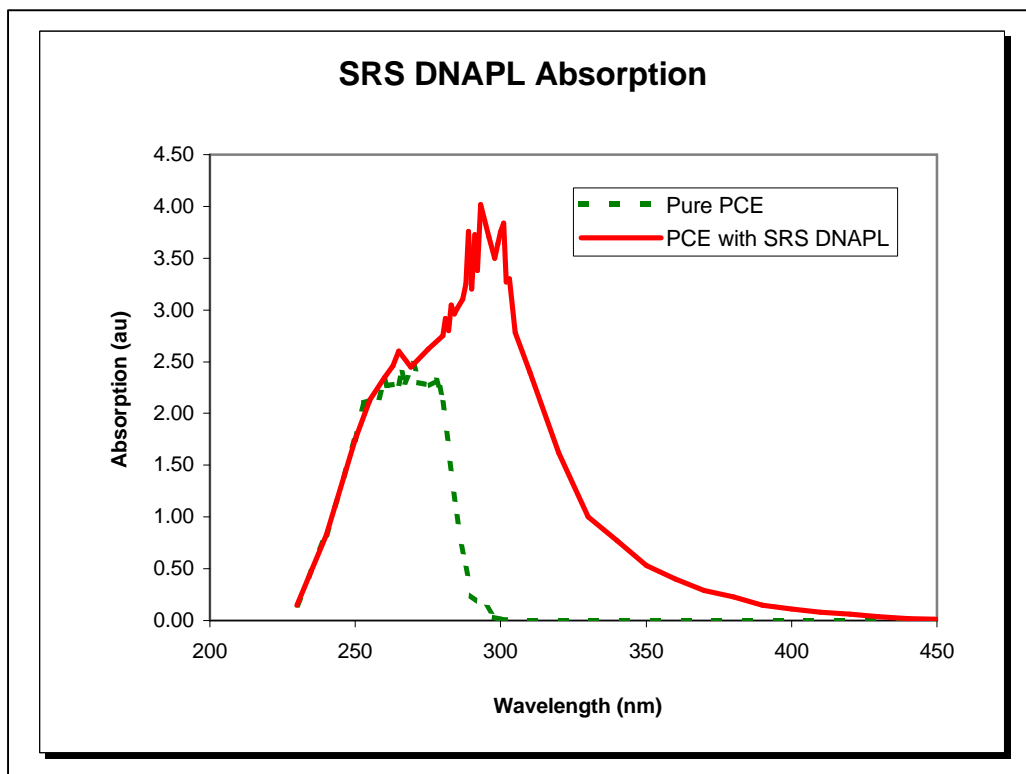
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Figure 4. Absorbance spectra of pure PCE and PCE mixed with SRS M-Area DNAPL, after Rossabi and Nave 1998.

The induced fluorescence emitted by PAHs is generally in a broad band from below 400nm to above 650nm depending on the excitation wavelength and the PAHs present. Certain excitation wavelengths can induce localized peaks in the fluorescence spectrum as well. For example, Figure 5, based on Rossabi and Nave 1998, compares fluorescence spectra of the SRS M-Area DNAPL stimulated with a low power, pulsed 337nm nitrogen laser and with a higher-powered mercury lamp. The 337nm laser-induced fluorescence shows hints of spectral features, particularly around 550nm, which are more prominent with the mercury lamp induced spectrum. Spectra induced by 365 and 405nm excitation (see Rossabi and Nave 1998 Figure 2) produce prominent features at 440, 480, 520, and 550nm; suggestions of these features at the three higher wavelengths are seen in Figure 5. Rossabi and Nave recommend analyzing samples of the oils and lubricants which have been used in the processes (e.g., metal fabrication followed by degreased using the suspected solvents) to aid in selecting optimal optical properties of the system to be deployed in any given application.

The fluorescence is transmitted to the surface via fiber-optic cable, processed, and recorded. The processing and recording can take place virtually continuously as the probe is pushed into the subsurface. Different systems process the fluorescence signal in different ways:

- The ROST™ system uses a digital oscilloscope to capture the fluorescence signal following the pulsed laser excitation. The system has the capability to capture fluorescence decay times in addition to signal strengths. This information would make it possible to discriminate between hydrocarbon and non-hydrocarbon fluorescence in most situations. It would be necessary to abandon continuous measurement as the probe is advanced in order to use this feature, however, so typically continuous measurements of total fluorescence and wavelength at which peak emission intensity is obtained are tracked as a function of depth during a continuous push.

- The FFD™ system uses filters to separate the fluorescence signal into a small number of frequency components, which enables discrimination among various classes of constituents. The latest version, the Dual Downhole FFD™, incorporates a pair of filters and photomultiplier tubes downhole, thus

avoiding the need for fiber-optic signal transmission with its attendant attenuation, particularly at lower wavelengths. Further information is available on ARA's web site.

- The SCAPS LIF system delivers the fluorescence signal to a spectrograph where it is dispersed spectrally onto a photodiode array. The resulting multidimensional signal is processed in real time to provide, for example, total fluorescence and peak wavelength. The entire spectrum can be stored for later processing. In addition, fluorescence decay information could be provided as well, to aid in contaminant identification; as with the ROST[TM], however, operation in this mode would require abandoning continuous tracking.
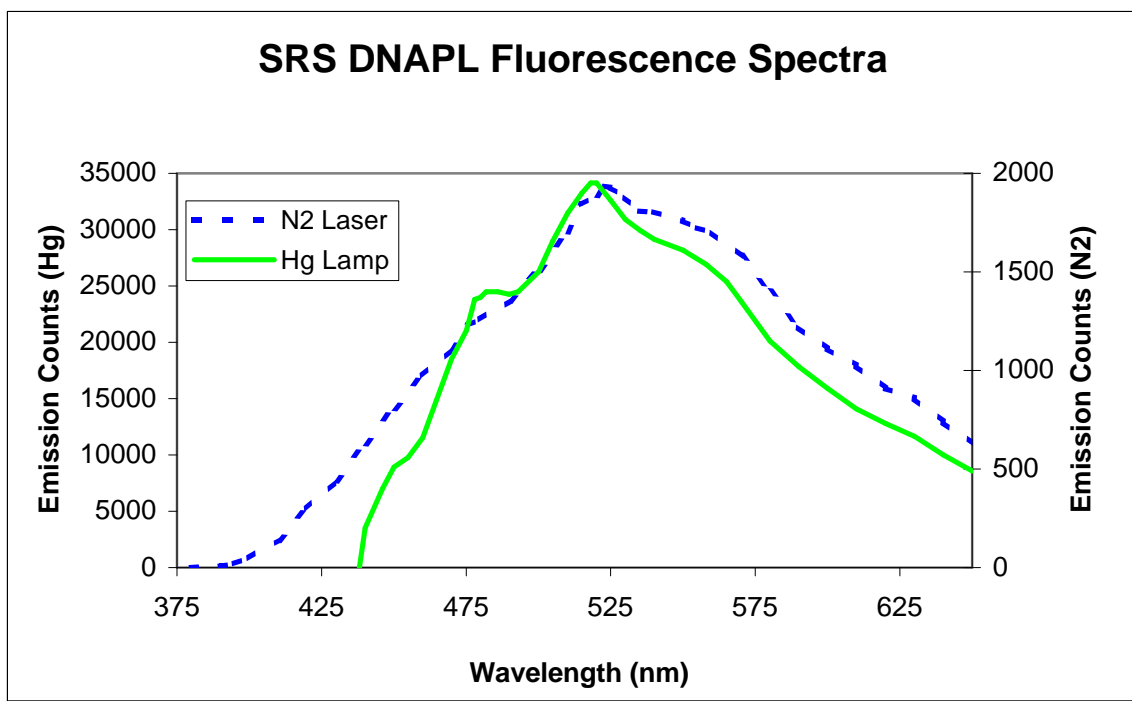

Figure 5. SRS M-Area DNAPL fluorescence spectra with low-power pulsed 337nm N$_2$ laser and higher-power Hg lamp illumination.
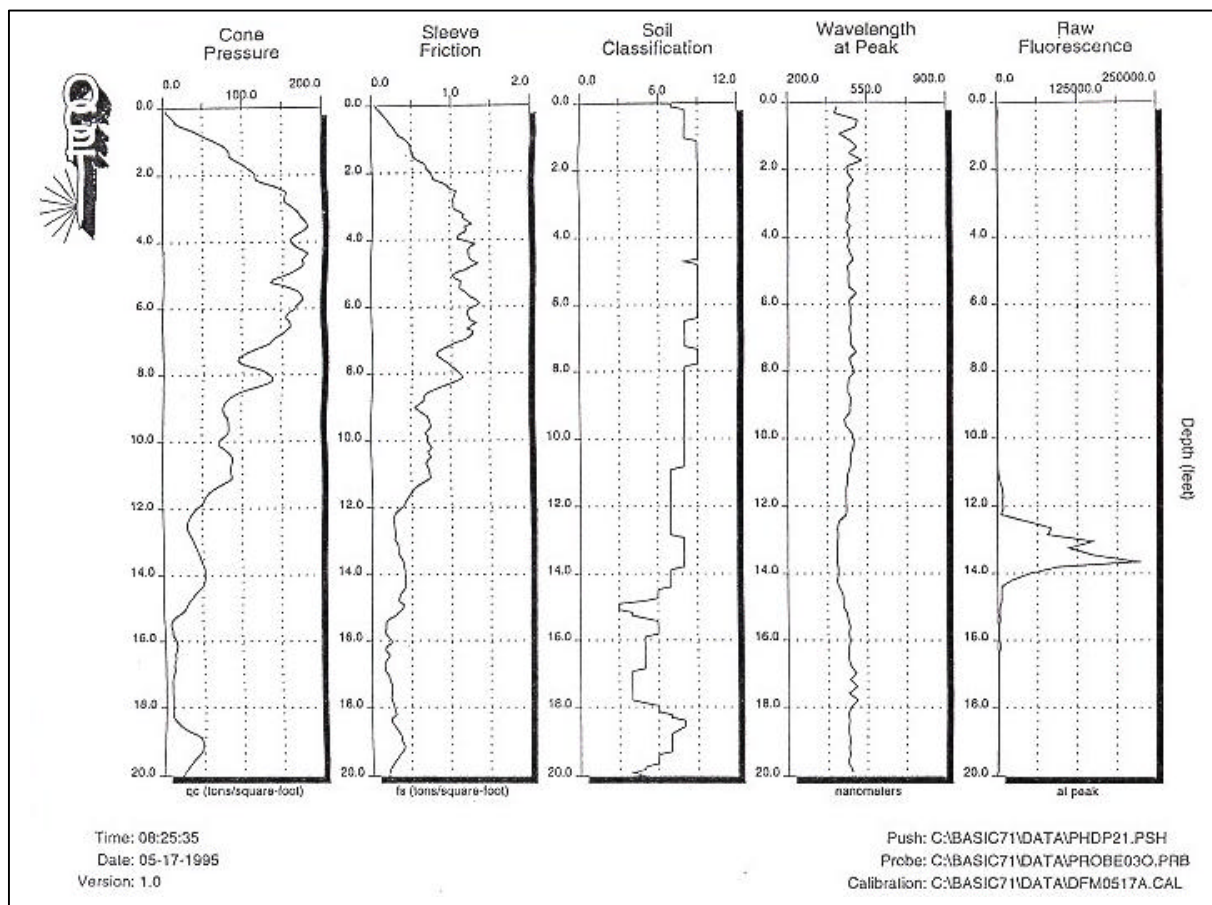
Figure 6. A combined geotechnical and total fluorescence display for the SCAPS-LIF sensor; from Bujewski and Rutherford 1997a.

All of these incorporate signal-processing software to provide graphs of total fluorescence and certain derived quantities as a function of depth. Figure 1 includes specimen logs for the ROST[TM] system. Additional examples may be found on the web sites of the respective vendors (www.fugro.com and www.dakotatechnologies.com for the ROST[TM] and www.vertek.ara.com for the FFD[TM]. With all systems data concerning the cone penetrometer or GeoProbe[TM] tip pressure, sleeve friction, and other parameters (for example, soil conductivity) can be collected, along with data from other sensors that may be deployed simultaneously. Figure 6, reproduced from Bujewski and Rutherford 1997a, is an example of such a chart produced using the SCAPS LIF system.

Note the vertical zone of elevated total fluorescence corresponding to a lowered peak wavelength, which aids in distinguishing contaminant from background signals. The dips in cone pressure and sleeve friction correspond to a finer-grained material just below the zone of contamination, which may serve as a vertical migration barrier. Subsequent analysis of the fluorescence spectra may be used to distinguish between fluorescence due to the target constituents and that due to interferents. Bujewski and Rutherford (1997a) report that both computer algorithms and human analysts had no trouble distinguishing hydrocarbon spectra from spectra produced by other materials such as calcium carbonate, resinous coal, Tide[TM] surfactant, norbergite, aragonite, Prestone[TM] antifreeze, fluorite, fossil algae, Simple Green[TM] detergent, scapolite, turritella agate, and quinine sulfate; moreover, organic constituents of soils produce minimal fluorescence which could interfere with the hydrocarbon signal in the SCAPS LIF spectra. These authors state (1997b) that the ROST[TM] system similarly allows for distinguishing hydrocarbon fluorescence from that of potential interferents.

System Operation

POL or NAPL plume delineation using induced fluorescence sensors with direct push systems typically follows this sequence:

- First one must determine that the constituents of concern are likely to fluoresce under ultraviolet illumination. This can be done through process knowledge: knowing what lubricants and/or cutting oils had been used and where DNAPL previously used in degreasing operations had been stored. Direct testing of constituents suspected of contaminating the subsurface is another option. The best option, not always available, is extracting known contaminants from the subsurface and testing them for fluorescence. The results of this testing can be used in selecting the sensor, excitation wavelength, and emission wavelengths to be used.

- The appropriate probe is then assembled into the direct penetration rod. Optionally, additional probes may be included which may aid in delineating or identifying constituents found, such as the Membrane Interface Probe (TechID 2950), the Cone Sipper (TechID 381), the Field Raman Spectrograph (TechID 873), or a downhole video camera such as the GeoVis™ (TechID 2399) or other video probe.

- Pushes are made at selected locations. Each push produces a record of fluorescence as a function of depth. Basic results such as total fluorescence and peak wavelength (or total fluorescence and time decay) are available in real time during each push; additional spectral information can be obtained soon thereafter. Continuous pushes proceed at rates up to one hundred feet or more per hour, and can reach depths of up to 150 feet or so (but recall the depth limitations inherent in transmitting shorter wavelength illumination through fiber-optics). The rods are steam cleaned as they are withdrawn from the holes, and the holes can be grouted as well. The total elapsed time for setting up at a location, sampling to a depth of sixty feet, withdrawing and cleaning the probe, sealing the hole, and moving to the next location is typically on the order of one to two hours.

- A great advantage of having basic results available in real time is that the sampling plan can be adjusted dynamically to make use of new information about contaminant extent as it becomes available. Also, other probes such as the Membrane Interface Probe (TechID 2950) can be used to investigate the chemistry of the downhole contamination in greater detail in locations where constituents of concern are suspected.

- Finally, data are logged and plotted. If desired, more careful analyses of the stored spectra can be made to identify and eliminate possible interferences, such as spectral contributions from naturally occurring minerals.

Each version of the induced fluorescence sensor has its own calibration and quality control procedures; see, for example, pages 30-31 of Bujewski and Rutherford 1997a for a discussion of those performed with the SCAPS LIF Sensor and pages 31-32 of Bujewski and Rutherford 1997b for those performed with the ROST™. Calibration and detection limit determination must be done for each application using the appropriate constituent of concern, since the fluorescence signal depends on the quantities and types of PAHs which are present for that particular application. Fluorescence intensity is also affected by soil type.

A two- or three-man crew of field technicians is used to operate the equipment. Power resources are self-contained within the cone penetrometer vehicle, and there are virtually no other consumables. The probe is cleaned and decontaminated upon removal from the subsurface, possibly creating modest amounts of secondary waste, although not directly from the subsurface. Aside from dealing with small amounts of potentially contaminated rinsate, there are no health or safety considerations beyond those typically involved in cone penetrometer operations.

Further information about these technologies and about the problems of locating and identifying DNAPL contamination in the subsurface can be found in numerous sources, including the following:

- Bujewski and Rutherford 1997a for the SCAPS LIF Sensor;

- Bujewski and Rutherford 1997b for the ROST[TM];
- U.S. EPA's *Field Analytical Technologies Encyclopedia* (FATE) online;
- Kenny 1999;
- Kenny *et al.* 2000;
- Kram 1998;
- Kram *et al.* 2001;
- Rossabi and Nave 1998; and
- Rossabi *et al.* 2000a, 2000b.

Future Enhancements

Three future enhancements of this technology should be mentioned. The first is the possibility of using multiple excitation frequencies simultaneously or sequentially, recording the response spectrum separately for each excitation frequency. Such a sensor is under development, called the Laser-Induced Fluorescence-Excitation-Emission-Matrix (LIF-EEM) probe; see Kenny 1999 and Kenny *et al.* 2000 for discussions. The LIF-EEM probe generates a two-dimensional matrix at each depth with each reading: fluorescence intensity at each of numerous wavelengths resulting from excitation using each of up to ten or so wavelengths. In principle the greater amount of information gathered will allow superior identification and simultaneous quantitation of individual constituents. As noted previously, however, the more energetic, shorter wavelength illumination is attenuated more rapidly by the fiber-optic cables, so this technology may be limited to shallower depths and will require depth-dependent calibration.

Another desirable future development would be the development of induced fluorescence systems deployable using direct push systems with smaller diameter rods or pneumatic hammer techniques, such as GeoProbe[TM] systems. ARA's Dual Downhole FFD[TM] boasts a cable with 0.35-inch diameter useful for this purpose.

Another advancement being testing is coupling the LIF system with the GeoVis. These technologies complement one another for enhanced contaminant detection.

SECTION 3
PERFORMANCE

Demonstration Plan

Demonstrations of the ROST[TM] and other DNAPL characterization technologies took place at the Savannah River Site during 1998 adjacent to the M-Area Settling Basin. The contamination associated with the M-Area Settling Basin involves waste chlorinated DNAPLs, specifically PCE and trichloroethylene (TCE) previously used in vapor degreasing operations, from leaky process sewer lines leading to the basin as well as from the basin itself. The geology adjacent to the M-basin is very well characterized. There is a very large dissolved solvent plume in this area; locally DNAPL has accumulated in the vadose zone in fine-grained clay-rich layers and on top of fine-grained zones below the water table. A significant concentration of solvent is in the vadose zone at a nominal depth of 100 feet directly adjacent to the basin; this is approximately the depth to which the cone penetrometer was able to penetrate. Free-phase DNAPL has been found in groundwater samples collected from groundwater wells located below the water table at this location.

Several pushes were made in the M-Area in the vicinity of soil borings. Pushes were completed to the impenetrable zone by cone penetrometer. For demonstration purposes, the cone penetrometer was withdrawn and conventional auger boring techniques were used to extend two of the borings to beneath the water table, after which the ROST[TM] was reintroduced. Soil core samples obtained every 0.5 feet in clay layers known to contain DNAPL were sent to an off-site laboratory for analysis. Total fluorescence logs, with associated soil concentrations of PCE and TCE, are presented in Figures 7, 8, and 9.
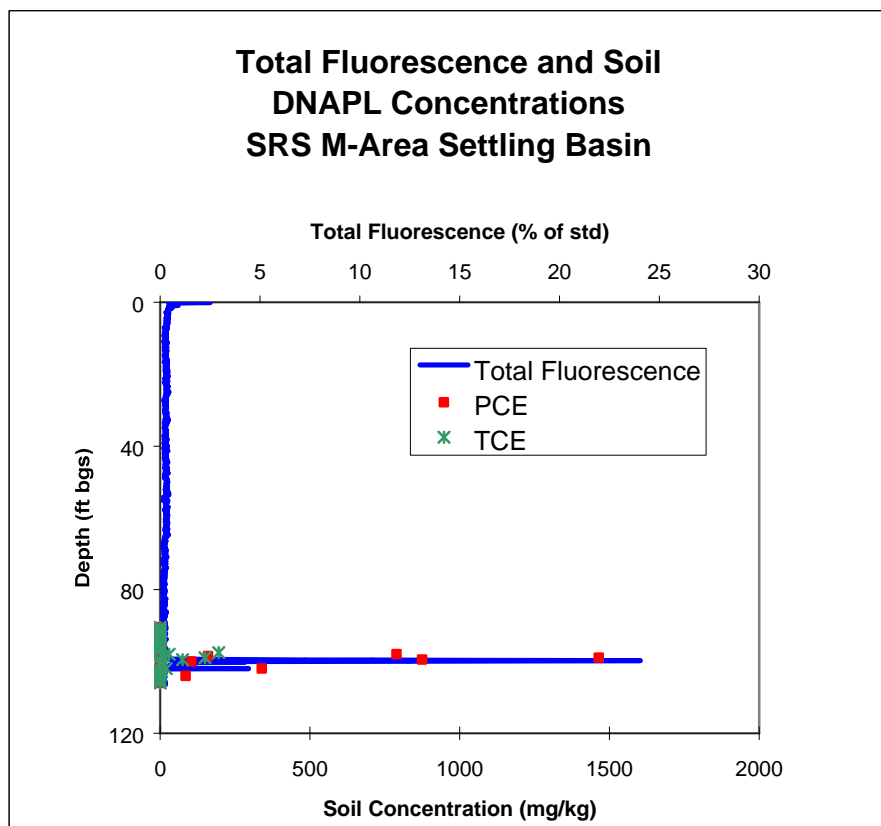

Figure 7. Total fluorescence as a function of depth compared with soil DNAPL concentrations, from the SRS M-Area Settling Basin.

Results

The results obtained in the M-Area Settling Basin show a close correspondence between soil core PCE and TCE measurements and regions of high fluorescence. There are two limitations to this comparison:

- The soil cores were obtained only every 0.5 feet, whereas the induced fluorescence results are virtually continuous. Given the discrete and heterogeneous nature of DNAPL contamination, the baseline core sampling technology may miss a DNAPL occurrence due to spatial limitations, although soil sampling and analysis remains more sensitive to dissolved contamination as well as quantities less that the induced fluorescence detection thresholds.

- The soil cores and cone penetrometer pushes were close to one another, but not at identical locations. The heterogeneity expected of DNAPL contamination suggests that one should not expect a complete correspondence between the results obtained at nearby but not identical locations.

Figures 7 and 8 show the comparative results for one of these pushes, which terminated at an impenetrable layer at 106'. Figure 7 presents the continuous reading of total fluorescence as a function of depth from the surface to the impenetrable zone, along with measured DNAPL (PCE and TCE) concentrations at the discrete depths at which soil cores were obtained. There is a clear correspondence between the soil concentrations and total fluorescence. Figure 8 shows an expanded view of the region with high fluorescence and detectable PCE and TCE concentrations. The offset of approximately one foot in depth between the highest fluorescence reading and the highest PCE concentration is likely due to local heterogeneities in DNAPL location along with the fact that the cone penetrometer push and soil core locations are close to one another but not identical. These data are taken from push ROST 2a and soil coring MSB3D at the SRS M-Area Settling Basin.
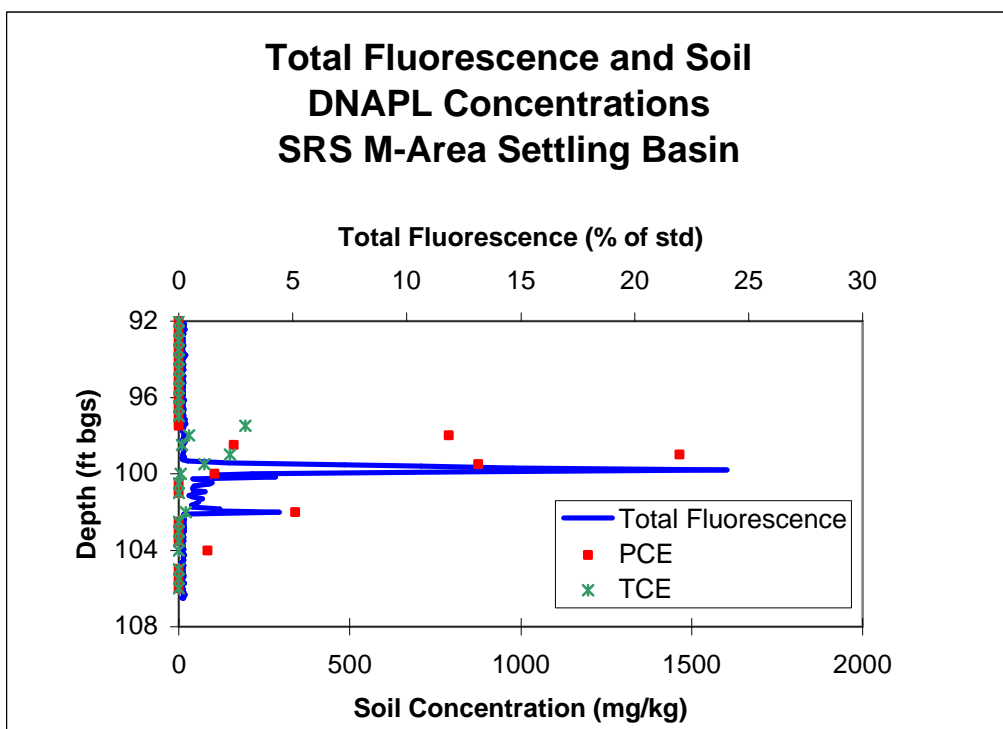

Figure 8. The region of interest in Figure 7 expanded.

Figure 9 shows the total fluorescence as a function of depth for one of the auger reborings (MHL03). The sensor was in the auger flights until a depth of 135 feet, in order to advance through the impenetrable (by

direct push) layer at 106'. The depth of the fluorescence peak corresponds to the depth of the screened zone of the well from which DNAPL was collected.

DNAPL PAH Fluorescence Near Water Table at SRS M-Area Settling Basin
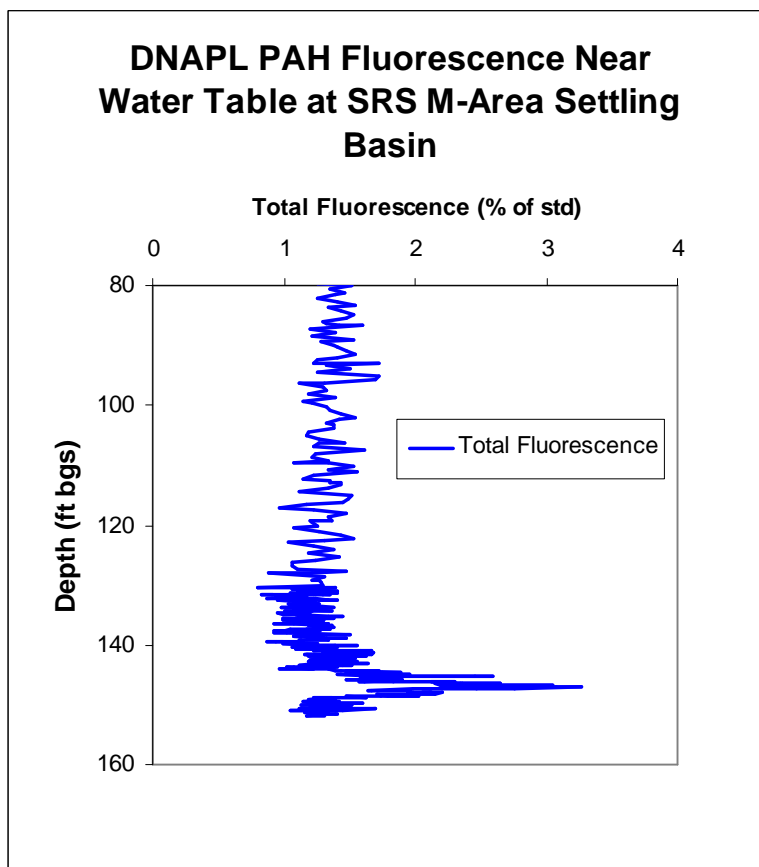
Figure 9. Total fluorescence as a function of depth. The sensor was in the auger flights to a depth of 135 feet. The depth of the fluorescence peak corresponds to the depth of the screened zone at the well from which DNAPL was collected.

Other Demonstrations

In addition to the M-Area Settling Basin demonstrations, DNAPL characterization approaches were demonstrated in the 321-M Solvent Storage Tank Area during 1998.   Unlike that of the M-Area Settling Basin, the contamination in the 321-M area is of unused PCE from a 1985 storage tank leak. Soil samples indicate the presence of separate phase solvent, but free product has not been bailed from wells as in the M-Area Settling Basin. The vadose zone geology here is less well characterized than that of the M-Area. Four pushes were made, to a depth of around 45 feet; cores were obtained in clay layers known to contain DNAPL and sent to an off-site laboratory for analysis. The laboratory analytical results were again compared with determinations made using the technologies being demonstrated. DNAPL is clearly present and identifiable by Raman spectroscopy (see Section 4), as discussed by Rossabi *et al.* 2000b. The absence of an induced fluorescence background in the Raman spectroscopy confirms conclusions from previous field tests of LIF sensors that induced fluorescence techniques are unable to detect pure DNAPL using feasible illumination wavelengths.

In addition to the demonstrations at SRS described above, there have been numerous other demonstrations of these and similar techniques, several of which are discussed in the references. In particular, the SCAPS LIF Sensor and the ROST[TM] were demonstrated by the U.S. EPA's National Exposure Research Laboratory (NERL) at the Naval Construction Battalion Center, Port Hueneme, CA and at Sandia National Laboratories, Albuquerque, NM during 1995. The target constituents in these demonstrations were POLs rather than DNAPLs; as discussed previously, the likelihood of success is far greater with POLs than NAPLs because of the ubiquitous presence of fluorescent PAHs in POLs.

These demonstrations were discussed in detail in two U.S. EPA *Innovative Technology Verification Reports* (Bujewski and Rutherford 1997a and 1997b). The conclusions are quite positive. Concerning the SCAPS LIF Sensor, the authors report the following:

- "Average percent agreement with conventional analysis for both sites was 94 percent correct with 1 percent false positives and 5 percent false negatives. ... Disagreements with the laboratory results were primarily confined to regions where contaminant concentration levels were close to the detection threshold."

- "Undoubtedly, it will be employed in a variety of applications, ranging from serving as a complement to data generated in a fixed analytical laboratory to generating data that will stand alone in the decision making process."

- "The technology offers a number of advantages over conventional ... techniques for the purpose of screening a site for the nature and extent of contamination. ... This information, when used properly, could provide a more complete picture of the contamination, and also could be used to predict future sampling locations."

They also report that the technology worked as well as or better than the developer claims.

Concerning the ROST^{TM} their conclusions are similar:

- "At Port Hueneme, the correlation with conventional TPH [Total Petroleum Hydrocarbon] analysis was 89.2% with 5.4% false negatives. At the Sandia tank farm, the TPH correlation was 93.4% with 3.3% false negatives. ... Any disagreements with the laboratory results were primarily confined to regions where contaminant concentration levels were close to the detection threshold."

- "As a screening technique to identify the nature and extent of aromatic hydrocarbon contamination, this technology has many advantages over conventional techniques."

Again, the authors report that the technology performed satisfactorily as claimed by the developers.

The demonstration of DNAPL characterization techniques at Launch Complex 34 at the Cape Canaveral Air Station has already been discussed. As at the SRS 321-M Solvent Storage Tank area, induced fluorescence techniques were unsuccessful at detecting subsurface DNAPL because of a lack of commingled POLs.

SECTION 4
TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing and Complementary Technologies

As discussed previously, induced fluorescence technologies perform well in general for locating non-aqueous phase POLs in the subsurface. For locating NAPLs there is no single superior technique; all techniques should be considered as complementary rather than competing. The SCFA approach of collecting several tools into the DNAPL Toolbox has been mentioned in Section 1. A few of these tools are discussed briefly here; see Kram *et al.* 2001 for a more extended discussion.

Raman Spectroscopy. This technique (TechID 873), developed for the DOE by EIC Laboratories, is similar to induced fluorescence spectroscopy in that the subsurface is illuminated at selected wavelengths and spectral analysis is performed on the resulting signal. The difference, technically, is that with induced fluorescence the PAH molecules are electronically excited (raised to a higher energy level), with resulting fluorescence emitted when they revert to their original energy states. With Raman spectroscopy the molecules shift the frequency of the stimulating light when it is scattered back toward the detector. The energy shifts in the scattered light are correlated with the vibrational modes of the particular molecule and constitute the Raman spectrum for that compound. There is a unique Raman spectrum for each molecule; hence Raman scattering can be used to identify specific contaminants in the subsurface. The Raman spectrum is best obtained using monochromatic laser light excitation.

The disadvantage is that the Raman spectra are several orders of magnitude weaker than induced fluorescence when the latter is present. To avoid induced fluorescence interference when it is present, Raman excitation wavelengths are typically longer (and hence lower energy) than those inducing fluorescence. Again, there is a trade-off between less interference and lower excitation energy when longer wavelengths are used. There can be situations where DNAPLs can be detected using Raman spectroscopy and not by induced fluorescence and vice versa (if a fluorophore is present in the DNAPL). Both types of systems can be deployed via the cone penetrometer. In fact, through judicious selection of excitation frequencies induced fluorescence imaging can be performed using the Raman system. Cone penetrometer-based Raman spectroscopy for DNAPL characterization is discussed by Rossabi *et al.* 2000b.

Also, it should be noted that the presence or absence of a fluorescence background to the Raman spectra is itself an indication of the nature of contaminants that may be present or absent in the subsurface.

Membrane Interface Probe (MIP). This cone penetrometer-based probe (TechID 2950), developed by GeoProbe^TM Systems, replaces the sapphire window on the probe with a membrane permeable to volatile organic constituents (VOCs) including DNAPLs. Vapor phase VOCs diffuse through the membrane and are transported to the surface for further analysis. The advantage of this technology is the identification of constituents found. However, this is not a continuously recording sensor as is the induced fluorescence probe, and hence is best used once a zone of suspected contamination has been identified. Kram *et al.* (2002) identify the MIP as a cost-effective DNAPL characterization tool. Recent developments that allow for near continuous screening using the MIP have the potential to make it even more cost-effective.

Cone Sipper. This cone penetrometer-based probe (TechID 381) allows the user on the surface to selectively sample soil liquids or gases at selected depths during a push. The liquids or vapors are brought to the surface using a gas lift pump; once on the surface, they are available for on-site or off-site chemical analyses. The cone sipper can be useful at identifying constituents detected by other means, such as induced fluorescence or GeoVis^TM. It is not, however, a continuously recording instrument like the induced fluorescence probe. The advantage of the Cone Sipper is that it allows collection of samples at multiple depths without removing and reinserting the cone penetrometer rod.

GeoVis^TM and Video Cone^TM. These are video cameras operating downhole via fiber optics (TechID 2399). The GeoVis^TM itself was developed by the Department of Defense; Applied Research Associates has developed a similar tool known as the Video-CPT^TM. Using these tools the operator on the surface can easily see variations in soil texture, structure, and moisture content. One can also see the discrete blobs and ganglia formed by non-aqueous phase liquids. Upon finding these one would call upon another

sensor to more closely identify the nature of the materials located. These sensors provide a continuous record of the subsurface.

Ribbon NAPL Sampler (RNS). This technology, developed by Flexible Liner Underground Technologies (FLUTe[TM], TechID 2238), consists of a hydrophobic membrane with a liner impregnated with a dye that changes color when it comes into contact with organic liquids. It can be deployed through a drill, cone penetrometer, or small diameter pneumatic hammer rod; alternately, it can be everted into a borehole by air pressure after the rod has been removed. Once the RNS has attained its maximum depth it is withdrawn using a string attached to the inside of the tip. The presence of organic liquids, including possible POLs or DNAPLs, is noted and the location measured from the membrane liner. Pieces of the liner can be excised for further chemical analysis to identify the constituents found.

This technology has proven very useful in locating suspected DNAPLs and, where DNAPL contamination is known to exist, in delineating its extent. It is not so specific as the induced fluorescence probe, and so is not limited to the situation where the contaminant is POL or DNAPL containing POL. On the other hand, its deployment is a two-step operation compared with the single step involved with either the induced fluorescence probe or the Raman spectroscopy probe.

Conventional Soil Sampling and Analysis. Collection of soil samples via hollow auger and split-spoon sampling is the baseline technology to which all of these innovative technologies are compared. The advantages of this technique are the positive identification of constituents of concern in the subsurface and the evaluation of the actual mean concentrations of those constituents in the volume of soil sampled, rather than in just the portion of soil adjacent to the particular innovative sensor; the latter is particularly relevant for DNAPLs present in discrete blobs and ganglia. Perhaps most importantly, conventional sampling and analysis is a well-understood technique that is universally accepted by regulators. The disadvantages are cost, delay until analytical results are known, and generation of secondary wastes. At least some conventional soil sampling and analysis will be performed during a typical investigation.

Technology Applicability

The prime application of induced fluorescence sensors is in screening for the presence and extent of subsurface contamination where the known or suspected contaminant consists of free-phase (not dissolved) POLs or NAPLs containing dissolved POLs. Since the sensor is deployed via a cone penetrometer or other direct push system, the subsurface layers sampled must allow for direct push sampling. Of course, boreholes could be created by other means after which the induced fluorescence probes deployed by cone penetrometer, so long as the subsurface media to be sampled will be in contact with the sapphire window on the probe.

Continuous records of subsurface fluorescence are typically produced; subsequent analysis of frequency or time spectra can be used to correct for possible fluorescence from interferents such as natural fluorescing minerals. Issues regarding the appropriate selection of illumination source have been discussed in Section 2. A minor complaint occasionally expressed is that the sapphire window is located at some distance behind the cone penetrometer tip, so that if a compact layer that also serves as a barrier to migration of DNAPLs impedes the push, the probe will not provide readings all the way to that barrier.

Patents/Commercialization/Sponsor

Commercialization

There are several commercial and non-commercial sources for this technology; some of these have been identified in Section 1. Variations in their implementation of the principles are described in Section 2.

SECTION 5
COST

Methodology

The cost analyses in this Section were prepared by MSE Technology Applications, Inc. (2000). The information used by MSE was supplied by SRS and by companies that commercially provide cone penetrometer services. Where possible, costs are cited as unit costs being averages of expenses obtained from two or more vendors. The baseline technology for detecting sediments contaminated with DNAPLs is core sampling using a hollow-stem, auger-drilling rig followed by off-site laboratory analysis.

This cost analysis is based on certain assumptions, representative of a vadose (unsaturated) zone investigation in an area similar to the M-Area Settling Basin at the SRS. These assumptions include the following:

- The suspected DNAPL contains PAHs capable of fluorescing.

- The region to be surveyed for suspected DNAPL contamination is hypothetically 90 feet by 300 feet; the zone to be investigated extends from 30 to 110 feet below ground surface; and there are no impediments to employing the direct push system.

- Five boreholes or CPT pushes will be required for proper characterization of this subsurface region. When the innovative technology is used, conventional samples will also be obtained from two boreholes.

Proper characterization of this site using the induced fluorescence probe would involve five direct pushes. In addition, two boreholes would be drilled to the same depth using a hollow-stem auger with sediment samples taken every two feet starting at the 30-foot level. These samples would be packaged and sent to the laboratory for DNAPL analyses to confirm the fluorescence probe findings. The baseline comparison involves conventional samples obtained every two feet starting at the 30-foot level in each of five boreholes.

Cost Analysis

The cost information provided here is taken from MSE (2000). A three-person crew is required for the induced fluorescence probe deployment, including technical oversight. The unit costs are provided in Table 5-1.

Table 5-1. Unit costs for the induced fluorescence probe deployment.

Description	Unit cost, $	Unit
CPT with induced fluorescence sensor	10.00	Foot
Grouting CPT hole	2.50	Foot
Mobilization and demobilization	750.00	Day
Per diem for three-person crew	255.00	Day
Standby labor rate	175.00	Hour
Decontamination labor rate	175.00	Hour

Table 5-2 gives unit costs of conventional sediment sampling followed by laboratory analysis.

Table 5-2. Unit costs for baseline sediment sampling and laboratory analysis.

Description	Unit cost, $	Unit
Hollow-stem auger	10.00	Foot
Split-spoon sampling	20.00	Sample
Grouting borehole	3.00	Foot
Mobilization and demobilization	1000.00	Day
Per diem for three-person crew	150.00	Day
Standby labor rate	170.00	Hour
Decontamination labor rate	100.00	Hour
Drilling waste disposal	36.50	Cubic foot
Laboratory analysis	144.00	Sample

Total costs for each scenario are given in Table 5-3.

Table 5-3. Comparison of total costs.

Category	Baseline	IF Probe
Drilling boreholes	5,500	2,200
Installing characterization tool	0	5,500
Grouting holes	1,650	2,035
Mobilization/demobilization	2,000	1,500
Standby	510	0
Decontamination	250	538
Sampling	4,100	1,640
Laboratory analysis	29,520	11,808
Waste disposal	1,369	821
Per diem	300	510
Total Cost	45,199	26,552

Cost Conclusions

In this hypothetical example the total cost for using the induced fluorescence technology was over 41% lower than that of the baseline technology. Even at that over 60% of the cost of the innovative technology deployment is associated with the two boreholes at which conventional (baseline) sampling followed by laboratory analysis was used to supplement the induced fluorescence probe data.   Hence the relative cost savings would be even greater with larger deployments using a greater number of total boreholes and/or pushes but the same number of confirmatory baseline samples.

Kram *et al.* (2002) present an additional cost comparison of eighteen different characterization approaches under a somewhat different scenario. They conclude that the induced fluorescence sensor deployed via cone penetrometer is the most cost-effect approach (where it works, of course), with a savings of around 53% over baseline costs with samples obtained only every five feet. Of course, the induced fluorescence sensors can be combined with other sensors in the same cone penetrometer push, obtaining complementary information. Two such combinations are considered by Kram *et al.*; these still provide a cost savings of 20% or more over baseline.

Additional benefits

In addition to the cost savings realized by using the induced fluorescence sensor with direct push system technology there are additional benefits, which have been mentioned previously:

- The availability of results in real time allows for dynamic sample planning; the results from one push can guide the location of subsequent pushes, toward the goal of delineating the extent of the plume of contamination. This is not possible using the baseline technology, since sample results are generally not available for at least several days following sampling.

- There is minimal secondary waste to be handled in the field. Secondary waste presents additional risk to personnel in addition to its disposal cost.

- There are no samples to be packaged and transported to off-site laboratories, hence avoiding cost, possible exposure, and the need to dispose of that form of secondary waste.

SECTION 6
REGULATORY AND POLICY ISSUES

Regulatory Considerations

Permits. No special permits are needed for use of the induced fluorescence sensors, except for any that might be needed for subsurface penetration in general.

Regulatory acceptance. The use of induced fluorescence sensors for delineation of POL contamination in the subsurface has become accepted standard practice; see ASTM 1997, Bujewski and Rutherford 1997a and 1997b, and U.S. EPA 1999. Its use in the detection and delineation of DNAPL contamination is more innovative, although a growing body of scientific literature and field experience supports it. The basic consideration for regulatory acceptance is whether, on a site-specific basis, the induced fluorescence sensor will reliably provide information needed for site characterization. This depends on the nature of the contamination present at the individual site, and must be demonstrated for each site before relying on induced fluorescence sensors to demonstrate an absence of DNAPL contamination.

Safety, Risks, Benefits, and Community Reaction

Community Safety. POL and DNAPL contamination are matters of serious concern, and remediation is mandatory at sites contaminated by these constituents. Given that POL and DNAPL characterization will be undertaken, direct push techniques such as the use of induced fluorescence sensors with direct push systems provide optimal safety and minimal exposure to secondary wastes. The only real consideration is to determine that the contaminants of interest at a particular site will indeed fluoresce; this determination avoids false negative findings that a subsurface region is free from contamination when in fact it is not.

Worker Safety. U.S. EPA has prepared a Standard Operating Procedure (SOP, U.S. EPA 1999) for the SCAPS/LIF implementation of the induced fluorescence sensor with a cone penetrometer. This SOP provides a general discussion of safety considerations. See also the ASTM Standard Practice D6187-97 (ASTM 1997).

In general, hazards due to exposure to potentially contaminated materials and generation of secondary waste are considerably reduced when induced fluorescence sensors can be deployed via direct push techniques from what they are with baseline technologies.

Environmental impact. No significant impact is anticipated from using these techniques. Boreholes and direct push holes are smaller in diameter than conventional well borings, and are grouted upon removal of the probes, so no additional migration pathways for contaminants are created.

Community reaction. The use of induced fluorescence sensors for direct push systems should have no socioeconomic impacts. Community reaction is expected to be favorable due to enhanced safety and reduced risk.

SECTION 8
LESSONS LEARNED

Technology Selection Considerations

The primary limitation on the use of this technology is in ensuring that the target constituents will in fact fluoresce when illuminated by UV light. This requires preliminary testing with the target constituent itself, obtained either from the source or from the subsurface. If the target constituent will fluoresce, these sensors have a great appeal for delineating the extent of the contaminant plume. In some cases, the nature of the target constituent may influence the selection of illumination wavelength or source.

A related consideration is that of matching the vendor to the nature of the problem. For applications in which the target constituents are POL, the technology is by now reasonably standard, and any of the major vendors will suffice. Where the target constituents include DNAPL the application is more innovative, however, and one should insist that a potential vendor have documented experience in the use of these technologies to maximize the potential for useable and interpretable results.

Another consideration is that the subsurface region to be evaluated should be amenable to penetration using direct push systems. The use of direct push systems can be augmented if necessary for penetrating compact layers; if this is necessary the cost savings associated with avoidance of drilling would be lost, but that associated with avoidance of laboratory analyses would remain.

Overall, a major conclusion is that no single technology will provide superior DNAPL characterization under all conditions. Rather, the investigator should be prepared to deploy any of a number of tools depending on site-specific conditions. The induced fluorescence probes are excellent and cost-effective tools for DNAPL characterization - when they work. If not, other potential tools are described in Section 4 and in several references; Kram *et al.* 2001, in particular, provide a comparison of the advantages and disadvantages of numerous approaches.

APPENDIX A
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